

STRUCTURAL FEATURES OF PRODUCTS DERIVED FROM WATER-ASSISTED LIQUEFACTION OF BITUMINOUS COALS

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INTRODUCTION

In recent years, several research teams interested in obtaining liquid fuels from coal have investigated approaches that involve adding substantial amounts of water with the coal during processing. Although the approaches taken by the different groups vary considerably, all groups cite the low cost of water -- as a reactant, extractant, or transport medium -- to be a potential advantage for aqueous liquefaction compared to more conventional processes. For some processes, the vapor pressure of water at reaction temperature makes a very considerable contribution to the total pressure required in the reaction section. Further research will show if the necessity of high pressure in aqueous systems can be avoided or if advantages in terms of product quality and yields realized through use of water will compensate for higher pressure requirements.

Work at our laboratory has investigated the interplay of organic solvent, water, and water-soluble catalysts on conversion of coal to soluble products in the presence of hydrogen gas [1,2,3]. At constant hydrogen partial pressure and temperature, conversion increases both with an increase in water density and an increase in water-to-coal ratio in the reactor. The mechanism by which water aids conversion is not known, but some experiments with deuterium oxide indicated that hydrogen-oxygen bonds in water were not being broken. In the presence of water, especially when a water-soluble molybdenum catalyst is also present, the full benefit of having an organic solvent present is achieved at solvent-to-coal ratios as low as 0.25. In addition, organic solvent, water, and catalyst are complementary in promoting conversion, and high conversions can be obtained by various combinations of these three aids to hydroliquefaction reactions.

These findings have led us to continue to conduct reactions with various combinations of coal-to-solvent and coal-to-water ratios, of temperature, and of hydrogen partial pressure. Our aim is to identify advantageous reaction conditions that may be used in a continuous process that employs a lower solvent-to-coal ratio for the feed stream than is used in current donor solvent processes. This work examines the structural features of coal liquids produced under a variety of unconventional reaction con-

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ditions. Some questions of interest are the following: For reaction at low solvent-to-coal ratios and high water partial pressure, do liquid products resemble those from conventional donor solvent processes, or take on some characteristics of pyrolysis products? Is there evidence of incorporation of oxygen from water in the products? What is the effect of reaction temperature on product characteristics? To examine these questions, reactions were carried out with two Illinois No. 6 bituminous coals, and the liquid products were extensively analyzed.

EXPERIMENTAL

Hydroliquefaction Reactions

Batchwise liquefactions of two Illinois No. 6 bituminous coals were carried out using varying values of organic vehicle-to-coal and water-to-coal in the charge. All reactions were carried out with use of a water-soluble catalyst, ammonium heptamolybdate, in the concentration range 0.08-0.27 wt% molybdenum on dry coal. Gaseous hydrogen was employed in all runs. Ultimate analyses of the two coals, Burning Star and River King, are shown in Table 1. Two different hydrogen-donor solvents were also employed in this work. A composite Lummus solvent was derived from the 2SCT series of experiments (LCF-9 runs) with Burning Star coal on the Lummus Integrated Two-Stage Liquefaction (ITSL) Process Development Unit. A second solvent, designated HWSRC, was resid from the hydrotreater at the Wilsonville Advanced Coal Liquefaction Facility, produced during Run 242 with Burning Star coal.

Table 1. Elemental and Ash Analyses (wt%) of Illinois No. 6 Coals.

	Burning Star		River King	
	mf	maf	mf	maf
H	4.74	5.47	4.65	5.27
C	67.5	77.9	65.2	73.9
O	--	(12.1) _{diff.}	--	(15.5) _{diff.}
N	0.8 ₆	1.0	0.9 ₆	1.1
S	3.0	3.5	3.7	4.2
Ash	10.6	--	13.8	--

Reactions were carried out in a stirred one-liter autoclave. Reaction conditions employed are shown in Table 2. Coal, organic solvent, water, and catalyst were charged batchwise. Hydrogen was charged cold to the reactor at the desired total reaction pressure. As the reactor temperature rose during the heat-up period, hydrogen gas was vented via a back pressure control valve to maintain the total pressure. During the course of the

reaction, the partial pressure of hydrogen decreased and that of other components increased. The total pressure and the hydrogen partial pressure at reaction temperature at the end of each run are shown in Table 2. In one run (H-14), the reaction was carried out under 1900 psig partial pressure of nitrogen. Reaction times were 30 or 60 minutes and were measured from the time the desired operating temperature was established. Following a reaction, the reactor was cooled overnight to room temperature. Product gases were vented to a gas holder, then metered and sampled. Light oils (n.b.p. $\leq 293^{\circ}\text{C}$) and water were stripped from the reactor by vacuum distillation. The remaining heavy liquids and solids were dissolved in toluene and removed from the reactor. The toluene was stripped from the heavy products that were subsequently analyzed for THF-, benzene-, and cyclohexane-insolubles to determine conversions and product distributions. Asphaltenes are defined as material soluble in benzene and insoluble in cyclohexane. Heavy oils are material soluble in cyclohexane.

Chemical and Instrumental Analyses

The vacuum-stripped products were separated into methylene chloride solubles and insolubles to facilitate further analyses. Elemental analyses were performed on both the methylene chloride soluble and insoluble portions. Molecular weight determinations were performed on methylene chloride solubles by vapor pressure osmometry. Quantitative measurements of phenolic O-H, and relative concentrations of N-H in the methylene chloride soluble fractions were made by near-infrared procedures. High resolution ^1H and ^{13}C NMR spectra of the methylene chloride soluble fractions were acquired on a Varian XL-100 spectrometer.

RESULTS

Solvent Analysis

Conversions to THF and benzene solubles, and yields of hydrocarbon products are shown in Table 3. Although all reaction conditions were not varied systematically, some general observations can be made. High THF conversions (greater than 90%) and high benzene conversions (approaching 90%) were achieved with both of the coal and solvent combinations tested, River King/Lummus and Burning Star/HWSRC. Use of low hydrogen pressure results in low THF conversions (Runs H-14 and H-17). With a low temperature, high THF conversions may be obtained, but benzene conversions are reduced (Runs H-12 and H-16). In systems with solvent present, high conversions are obtained both with and without added water, but at lower pressure when water is absent (Runs H-10, H-24, and H-30).

Elemental Analyses of Feed and Product Fractions

Table 1 shows that analyses of the two coals are very similar, as expected. Tables 4 and 5 give the elemental analyses and average molecular weight of the methylene chloride soluble and insoluble fractions, respectively, of the two solvents used -- composite Lummus ITSL solvent and hydrogenated Wilsonville thermal resid (HWSRC). Essentially all the HWSRC is soluble in methylene chloride. The tables disclose several significant

Table 2. Experimental Reaction Conditions Associated with Liquefaction Products Analyzed

Autoclave Run No.	Added Solvent	Solvent/ Coal	Water/ Coal	Catalyst wt% Mo on Coal	Temp. (°C)	Time (min.)	Final Pressure, psig	
							P _{Total}	P _{H₂}
H-10	Lummus	0.33	0.25	0.14	427	60	4250	1750
H-12	None	0	0.44	0.10	370	30	4050	1760
H-14	Lummus	0.33	0	0.27	427	60	4510 (3160 N ₂)	520
H-16	Lummus	0.33	0.25	0.08	370	60	4690	2820
H-17	None	0	0.44	0.10	427	60	3880	720
H-24	HWSRC	0.33	0	0.10	427	60	2170	1530
H-30	HWSRC	0.33	0	0.10	427	60	1730	1180

All runs with Illinois No. 6 coal -- River King (H-10 through H-16) and Burning Star (H-17 through H-30).

Table 3. Conversion to Solubles and Yields in Liquefaction Experiments

Autoclave Run No.	Conversion (wt%, maf Coal)		Net Yield (wt%, maf Coal)			
	THF	Benzene	Asphaltenes	Heavy Oils	Light Oils	Hydrocarbon Gases
H-10	90.2	87.6	17.7	66.7	9.0	8.7
H-12	89.7	55.0	29.7	17.9	1.0	---
H-14	71.9	59.8	16.7	43.8	9.0	7.1
H-16	92.7	66.2	42.1	37.7	3.0	---
H-17	84.1	----	38.0	11.8	3.8	5.3
H-24	91.4	86.6	27.2	68.0	8.6	6.3
H-30	90.8	83.9	28.6	59.7	10.6	5.5

Table 4. Elemental Analyses and Number Average Molecular Weights of Methylene Chloride Soluble Fractions of Solvents and Heavy Aqueous Liquefaction Products.

Sample	C	H	O	N	S	H/C	\bar{M}_n^a
Composite Lummus ITSL Solvent	90.4	6.9 ₃	1.5	0.7 ₀	0.4 ₃	0.91 ₃	345
HWSRC Solvent	89.6	7.4 ₆	1.9	0.8 ₃	0.2 ₇	0.99 ₀	587
H-10	88.5	7.4 ₆	2.6	1.1	0.3 ₃	1.0 ₀	315
H-12	84.1	7.2 ₇	6.0	1.1	1.5 ₇	1.0 ₃	573
H-14 ^b	89.4	6.6 ₃	2.3	1.2	0.5 ₀	0.88 ₈	318
H-16	86.4	7.2 ₈	4.2	1.1	1.0 ₃	1.0 ₀	408
H-17	87.8	7.1 ₀	3.2	1.4	0.5 ₂	0.96 ₄	340
H-24	88.8	7.4 ₇	2.4	1.1	0.3 ₁	1.0 ₀	343
H-30	89.0	7.0 ₃	2.3	1.3	0.3 ₃	0.94 ₁	362

^aAVPO in pyridine @ 80°C.^bAverage of two determinations.

Table 5. Elemental Analyses (C,H,N) of Methylene Chloride Insoluble Fractions of Solvents and Heavy Aqueous Liquefaction Products on an Ash-Free Basis.

Sample	C	H	N	H/C
Composite Lummus ITSL Solvent	86.4	4.9 ₄	2.1	0.68 ₂
H-10	74.8	4.5 ₂	2.4	0.72 ₀
H-12	81.3	5.7 ₆	1.5	0.84 ₄
H-14	85.4	4.2 ₄	1.6	0.59 ₁
H-16	80.8	5.8 ₃	1.6	0.85 ₉
H-17	89.6	4.9 ₈	1.9	0.66 ₂
H-24	87.7	5.1 ₇	2.1	0.70 ₂
H-30	88.1	5.0 ₀	2.2	0.68 ₁

differences between the solvents. The Lummus solvent is of lower molecular weight and is less hydrogenated. The average molecular weight of the HWSRC is in the range expected for soluble nondistillate coal-derived resids.

Tables 4 and 5 also contain elemental analyses for the methylene chloride soluble and insoluble fractions, respectively, of the residual reaction products after the light oil has been stripped off. The hydrogen content of the methylene chloride soluble fractions of the products is ~7%, similar to that of the added hydrogen donor solvents. Although the relative yields of methylene chloride solubles are considerably reduced in the runs made at 370°C vs. 427°C, the H/C ratio of the solubles does not appear to be highly temperature dependent. All of the methylene chloride solubles are higher in oxygen than the added hydrogen donor solvents (which have been catalytically hydrotreated). The oxygen content of the products from the runs at 370°C is considerably higher than that of the runs at 427°C. However, excluding the 30-minute Run H-12 with added solvent in which poor conversion to methylene chloride solubles was achieved, the oxygen determinations in Table 4 are in the range expected for conventional direct liquefaction products of similar average molecular weight derived from Illinois No. 6 coal.

Heteroatomic Functionality

Infrared analyses of the O-H and N-H functionality in the solvents and heavy products are summarized in Table 6. The fraction of oxygen present as phenolic OH in the methylene chloride solubles appears to be between 0.3 and 0.4, and follows the total oxygen in Table 4 as determined by elemental analysis. The results reflect the fact that hydrogenolysis of carbon-oxygen bonds is less extensive at 370°C than at 427°C. Also, the methylene

Table 6. Dilute Solution Infrared Analyses of Methylene Chloride Soluble Solvent Fractions and Product Fractions

Solvent	%O as Free OH	Fraction of Total O as Free OH	Est.% N as N-H	Fraction of Total N as N-H
Composite Lummus ITSL	0.4 ₇	0.3 ₂	0.2 ₅	0.3 ₆
HWSRC	0.4 ₄	0.2 ₃	0.2 ₈	0.3 ₄
Autoclave Run No.				
H-10	0.9 ₇	0.3 ₇	0.3 ₂	0.3 ₀
H-12	1.7	0.2 ₉	0.2 ₀	0.1 ₉
H-14	0.8 ₈	0.3 ₅	0.4 ₄	0.4 ₀
H-16	1.3	0.3 ₂	0.2 ₇	0.2 ₅
H-17	1.5	0.4 ₇	0.4 ₈	0.3 ₅
H-24	0.9 ₉	0.4 ₁	0.4 ₃	0.4 ₀
H-30	0.9 ₄	0.4 ₁	0.4 ₄	0.3 ₄

chloride solubles from runs made without added hydrogen donor solvent tend to be higher in phenolic O-H and oxygen than from runs made with added solvents that are relatively depleted in oxygen. The estimated fraction of the nitrogen present as pyrrolic N-H is from 0.3 to 0.4, values that are consistent with similar infrared analyses of other direct liquefaction products derived from Illinois No. 6 (Burning Star) coal.

Average Structural Parameters

As a means of further comparing the heavy dewatered products, average structural parameters associated with the methylene chloride soluble solvent and product fractions have been calculated. These parameters should not be viewed as a means of constructing fictitious "average structures" for these very complex fractions but as a means of condensing a large body of diverse information into a set of correlative parameters that may prove useful for comparing samples and drawing general conclusions.

The mean structural parameters tabulated in Table 7 have been calculated by the Brown and Ladner procedure⁴ from elemental analysis, ¹H NMR, and NIR data. The aliphatic H/C ratio was assumed to be two for all groups having proton resonances in the H_α and H_β regions, and three for groups

Table 7a. Mean Structural (Brown and Ladner) Parameters of Methylene Chloride Soluble Fractions of Hydrogen Donor Solvents

	Solvent	
	Composite Lummus ITSL	HWSRC
Carbon Aromaticity, f_a	0.73	0.62
Hydrogen Aromaticity, H_{ar}^*	0.37	0.20
Degree of Aromatic Ring Substitution, σ	0.30	0.49
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.64	0.61
Average Alkyl Substituent Chain Length, n	2.2	2.2

(mostly methyl) having resonances in the H_γ region. This "prescription" generally yields calculated aromaticity values for bituminous coal liquefaction products that agree with the direct ^{13}C NMR measurements.

The mean structural parameters of the added donor solvents are given in Table 7a. The calculated aromaticities reflect the relative hydrogen content of the solvents as determined by elemental analysis (Table 4). The degree of aromatic ring substitution (σ), which is an estimate of the fraction of aromatic ring edge atoms bearing a substituent, is higher for more hydrogenated HWSRC. In part, this is a consequence of the fact that the Brown and Ladner approach treats hydroaromatic rings as two alkyl substituents with an average carbon chain length of two. In both solvents, the estimated average alkyl substituent chain length is about two, i.e., in common with most heavy coal liquefaction products, the most prominent alkyl substituents are methyl groups and hydroaromatic rings as opposed to long chain alkyl groups. The calculated H/C ratio of the unsubstituted aromatic units (H_{aru}/C_{ar}) imply that the average aromatic units in both solvent fractions are larger than three rings and that the average size of such units is larger in the HWSRC than in the methylene chloride soluble fraction of the composite Lummus ITSL solvent. However, it should be realized that this parameter is an insensitive indicator of the exact ring cluster size for systems containing more than three aromatic rings. In addition, since the Brown and Ladner treatment does not acknowledge the presence of heterocyclic rings, care should be exercised in attaching more than qualitative significance to these results.

None of the structural parameters characterizing the methylene chloride soluble fractions of the heavy dewatered aqueous liquefaction products (Table 7b) are significantly different from those of direct liquefaction products of similar hydrogen content and molecular weight range derived from Illinois No. 6 coal. As an example, analyses of two light thermal resid

Table 7b. Mean Structural (Brown and Ladner) Parameters of Methylene Chloride Soluble Product Fractions Calculated Using $^1\text{H-NMR}$ Data

	Autoclave Run No.						
	H-10	H-12	H-14	H-16	H-17	H-24	H-30
Carbon Aromaticity, f_a	0.68	0.62	0.76	0.66	0.69	0.67	0.70
Hydrogen Aromaticity, $H_{ar}^\#$	0.34	0.22	0.45	0.27	0.33	0.30	0.33
Degree of Aromatic Ring Substitution, σ	0.33	0.48	0.27	0.39	0.33	0.37	0.36
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.76	0.70	0.72	0.68	0.68	0.71	0.69
Average Alkyl Substituent Chain Length, n	1.9	2.0	1.7	2.1	2.2	2.0	1.9

(LTR's) from Non-Integrated Two-Stage Liquefaction (NTSL) experimentation at Wilsonville are summarized in Table 8. In Run 236 the dissolver was operated under "mild" severity NTSL conditions (419°C, 2000 psig H_2 , 30 lb/hr ft^3 coal space rate), while in Run 241 the dissolver was operated under "moderate" severity NTSL conditions (430°C, 2400 psig H_2 , 20 lb/hr ft^3 coal space rate). The aqueous liquefaction fractions tend to be only slightly lower in average molecular weight and slightly more hydrogenated than the light thermal resid from NTSL Run 236. After allowing for the diluting effect of the added donor solvent, the percent oxygen appears to be slightly lower in the aqueous liquefaction product fractions than in the LTR's, but the fraction of oxygen as OH is similar in both cases. Likewise, the estimated wt% nitrogen as pyrrolic N-H and fraction of the total nitrogen as N-H are similar for both types of products.

Table 8a. Elemental Analyses and Number Average Molecular Weights of Methylene Chloride Soluble Fractions of Light Thermal Resids from Liquefaction of Illinois No. 6 (Burning Star) Coal at the Wilsonville ACLTF.

Run No.	Elemental Analysis (wt%)					H/C	\bar{M}_n
	C	H	O	N	S		
236	85.1	6.7 ₀	5.5	1.6	1.1	0.938	464
241	88.1	6.1 ₉	3.3	1.6	0.8	0.836	453

Table 8b. Near-Infrared Analyses of Methylene Chloride Soluble Fractions of Light Thermal Resids.

Run No.	% O as Free OH	Fraction O as Free OH	Estimated %N as NH	Fraction N as NH
236	1.8 ₆	0.3 ₇	0.4 ₄	0.3
241	1.4 ₂	0.4 ₆	0.5 ₁	0.3

Table 8c. Mean Structural (Brown and Ladner) Parameters of Methylene Chloride Soluble Fractions of Light Thermal Resids.

	Light Thermal Resid	
	Run 236	Run 241
Carbon Aromaticity, f_a	0.70	0.75
Hydrogen Aromaticity, H_{ar}^*	0.32	0.35
Degree of Aromatic Ring Substitution, σ	0.38	0.36
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.69	0.61
Average Alkyl Substituent Chain Length, n	1.8	1.7

DISCUSSION

From the viewpoint of general structural features such as aromaticity, hydrogen distribution, and heteroatom functionality, the methylene chloride solubles of the vacuum-stripped products from aqueous liquefaction of Illinois No. 6 coal in the presence of added Mo catalyst are remarkably similar to conventional direct liquefaction products of the same molecular weight range derived from this coal. They do not exhibit features characteristic of coal pyrolysis products, such as a predominance of highly condensed polycyclic aromatic structures with a low degree of ring substitution and low phenolic content. These results are consistent with recent reports of the product composition from dissociation of Illinois No. 6 coal in base-catalyzed CO and H₂O systems.⁵ In the latter experiments, no dramatic differences in composition of the toluene soluble product fractions were found over a wide range of conversion. Also, chromatographic profiles of the toluene solubles from liquefaction of Illinois No. 6 coal in CO and H₂ and in tetralin were similar, although the mechanism of coal dissociation in the two systems must be quite different. A distinction has been made

between thermal severity (temperature, residence time) and reduction severity (specific reactivity of the reducing species). The inference has been made that similar weak bonds in the coal macromolecular structure are being broken in both aqueous and conventional coal liquefaction systems and that the products reflect some statistical regularity or uniformity in the distribution of chemical entities that constitute the coal macromolecular structure. Thus, although increasing the reduction (chemical) severity may increase the rate of bond breaking by chemical rather than thermal mechanisms, the observed result is primarily a larger number of liberated fragments rather than a change in their character. The present work indicates a similar interpretation is consistent with the reaction systems studied here.

In the present experiments, temperature is the most obvious variable influencing both yields and product composition. There appears to be the same trade-off in the aqueous liquefaction of catalyst-impregnated coal as in conventional thermal liquefaction using hydrogen donor solvents without added catalyst. Lower reaction temperatures ($<400^{\circ}\text{C}$) tend to favor hydrogenation over cracking and result in reduced hydrocarbon gas production, lower distillate yields, and higher yields of heteroatom-rich resid that may be soluble in polar solvents. Higher reaction temperatures ($>400^{\circ}\text{C}$) favor thermolysis and hydrogenolysis over hydrogenation. A higher yield of distillate may result, but the remaining resid tends to become more refractory in nature, and the production of light hydrocarbon gases increases.

The chemical role of the water, if any, in the catalyst-impregnated coal and aqueous liquefaction system is not clear from the elemental and structural analyses of the products. Use of water as a vehicle with added ITSL solvent and catalyst appears to have given no better results than hydrogenation of the catalyst-impregnated coal in the presence of small quantities of a heavier, slightly more hydrogenated solvent at moderate pressures. There is no evidence for any significant net incorporation of oxygen; the water-assisted liquefaction products are not any higher in total oxygen or phenolic OH than conventional thermal-stage coal dissociation products of Illinois No. 6 coal.

In terms of H/C ratio, and carbon and hydrogen aromaticities, the methylene chloride soluble fractions of the residual liquefaction products exhibit characteristics typical of donor solvent liquefaction products. As seen in Table 7, except for Run H-14, the aromaticities of the reaction products were less than that of the Lummus ITSL solvent and comparable to that of the HWSRC. Table 8c discloses that the carbon and hydrogen aromaticities of light thermal resids produced at Wilsonville in NTSL Runs 236 and 241 are higher on average than those for the reaction products of this work. The analytical data indicate that the latter products have properties typical of similar molecular weight products that were produced in conventional donor solvent processes.

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